Epitaxial Growth of $FeSe_{0.5}Te_{0.5}$ Thin Films on CaF_2 Substrates with High Critical Current Density

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In-situ epitaxial growth of $FeSe_{0.5}Te_{0.5}$ thin films is demonstrated on a nonoxide substrate CaF_2. Structural analysis reveals that compressive stress is moderately added to 36-nm-thick $FeSe_{0.5}Te_{0.5}$, which pushes up the critical temperature to above 15 K, showing higher values than that of bulk crystals. The critical current density at T = 4.5 K reaches 5.9 × 10^4 Acm^{-2} at $\mu_0 H$ = 10 T, and 4.2 × 10^4 Acm^{-2} at $\mu_0 H$ = 14 T. These results indicate that fluoride substrates have high potential for the growth of iron-based superconductors in comparison with popular oxide substrates.

Since the discovery of iron-based superconductors,[1)] much effort has been devoted to establish a thin-film growth technique of these compounds.[2–8)] At an early stage, iron-chalcogenide superconductors[9)] had been considered rather inappropriate for practical applications simply because of their low critical temperature (T_c). However, pressure-effect studies demonstrate that the potential T_c of iron-chalcogenide superconductors is as high as 37 K,[10,11)] which motivated us to begin the study of thin-film growth of $FeSe_{1-x}Te_x$. Through many reports,[12–16)] one problem has gradually emerged; There is a close correlation between T_c and the structure of the films grown epitaxially, but their lattice parameters are influenced by too many growth parameters, and the lattice parameters of the substrate material are not a dominant factor.[17–19)] In other words, $FeSe_{1-x}Te_x$ can be grown epitaxially on a single-crystalline substrate, but the lattice parameters cannot be designed in accordance with those of the substrates. One of the possible reasons that we have previously proposed for this is oxygen contamination from oxide substrates,[18,19)] and we actually confirmed the presence of oxygen at the interface of $FeSe_{1-x}Te_x$ grown on YSZ and $LaSrAlO_4$. In order to avoid this problem and further improve superconducting properties, it is important to investigate the film growth

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on nonoxide substrates. In this Letter, we demonstrate an epitaxial growth on nonoxide single-crystalline substrates, CaF_2 (a_0 = 5.463 Å). Our results indicate that films with high-T_c and high-J_c can be obtained reproducibly on CaF_2 (100) substrates even with a thickness as small as approximately 40 nm. Several films showed a T_c higher than that of bulk single crystals, strongly suggesting that the epitaxial strain effect moderately works on CaF_2 (100).

All the films were grown by pulsed laser deposition from an $FeSe_{0.5}Te_{0.5}$ target, as was described elsewhere.[16,18,19] Substrate temperature, laser repetition rate, and back pressure are 280°C, 10 Hz, and $\sim 10^{-5}$ Torr, respectively. Commercially available CaF_2 (100) substrates were used for the present experiments. A specially designed metal mask was put directly on the substrate to make the films into a six-terminal shape, in which the dimensions of the measured area are 0.95 mm length and 0.2 mm width. We prepared four very thin films with thicknesses of approximately 40 nm named C1 (36 nm), C2 (38 nm), C3 (40 nm), and C4 (42 nm), and two relatively thick films with thicknesses of approximately 150 nm named C5 (150 nm) and C6 (175 nm). The resistivity and critical current were measured using a physical property measurement system (PPMS) under magnetic fields of up to 14 T.

All the films are c-axis oriented as shown in Fig. 1(a), and no reflections originating from an impurity phase are detected. In-plane orientation is confirmed for C1, C3, and C5 by a 4-circle diffractometer. Figure 1(b) shows the ϕ scans of the 101 reflection of $FeSe_{0.5}Te_{0.5}$ and the 115 reflection of CaF_2 in film C1. A 4-fold symmetry reflection is obtained as observed in the films on several oxide substrates,[18] and we can identify the in-plane orientation as $FeSe_{0.5}Te_{0.5}$ [100] $\parallel$ CaF_2 [110]. It should be noted that the peak width of the 101 reflection is comparable to but not better than that reported in the film prepared on $LaAlO_3$ as shown in Fig. 1(c); FWHM of the peak is $\approx 1.0°$ for C1 showing a larger value than reported for the film on $LaAlO_3$.[18] Figure 1(d) shows the cross-sectional TEM image of film C5 at the interface. Roughness of the boundary looks to be more emphasized when compared with the case of $LaAlO_3$ substrate,[18,19] but no amorphous layer is observed between the film and the substrate.

The calculated c- and a-axis lengths are summarized in Fig. 1(e); the former is calculated from position of the 001 - 004 reflections, and the latter is determined from the position of 101 and the calculated c-axis length. The c-axis lengths of all the films exceed 5.94 Å, and are longer than that reported for the films grown on oxide substrates in our previous paper.[18,19] The a-axis lengths of three films show correspondingly short values, less than 3.78 Å, which are comparable with those reported by Bellingeri *et al.*[17] Thus, it is concluded that these films are compressed along the a-axis and are elongated simultaneously along the c-axis. Note that such a short a-axis length of the film is not due to a simple coincidence to the lattice parameters of CaF_2 ($a_0/\sqrt{2}$ = 3.863 Å). The reason why the a-axis is so strongly compressed has not yet been clarified, and we can only speculate on a possible chemical reaction between

$FeSe_{1-x}Te_x$ and F and/or some unknown mechanisms in $FeSe_{1-x}Te_x$ to shrink the a axis in oxygen-free environment.

The temperature dependences of resistivity of the six films are summarized in Fig. 2(a). All the films exhibit a higher T_c than those in our previous works.[18,19] T_c's are concentrated within a narrow temperature region around 15 K with high reproducibility, even though the normal state resistivities are rather scattered. The observation of the less-scattered T_c's shows a clear contrast to the results of the films on various oxide substrates.[18,19] Among the six films, C1 and C5 are remarkable for their T_c's exceeding 14 K, which is the highest T_c value reported for $FeSe_{1-x}Te_x$ single crystals in ambient pressure; the midpoint T_c (T_c^{mid}) and zero-resistivity T_c (T_c^{zero}) are 16.1 and 15.2 K for C1, and 16.3 and 15.3 K for C5, respectively. This is not the first example, and a higher T_c (onset) of 21 K has been already reported by Bellingeri *et al.*[17] However, they have obtained such a high T_c only in relatively thick films of 200 nm. We emphasize in the present study that even a far thinner film can exhibit a higher T_c than bulk crystals, and we are sure that this is one of the significant benefits of using a CaF_2 oxygen-free substrate. In particular, when fabricating SNS Josephson junctions and SIS tunnel junctions, it becomes very important to prepare a sharp interface between superconductors and normal metals and/or barrier insulators. For that purpose, thinner film have an advantage of smoother surfaces than thicker films, and we believe that CaF_2 will work as one of the promising substrates.

These films show remarkable properties also in a magnetic field. Figure 2(c) shows a suppression of T_c by applying magnetic fields along the c-axis direction ($H \parallel c$).[20] Even under 14 T, the decrease of T_c^{mid} is less than 2 K, and thus the upper critical field (H_{c2}) is suggested to be high. However, H_{c2} at the region close to T_c is not linear to T suggesting that an application of the WHH relation to the present case is invalid. With a simple application of the WHH relation to estimate H_{c2} using $H_{c2}(0)$ = - $0.69T_c(dH_{c2}/dT)|_{T=T_c}$, we obtained H_{c2} = 120 T. This is obviously overestimated, and the actual H_{c2} must be less than this value. However, even if we use a linear extrapolation of the tangential line at $\mu_0 H = 14$ T instead, and multiply 0.69 to the value at T =0 K, we obtain H_{c2} = 74.5 T, which is still larger than those reported for $FeSe_{0.5}Te_{0.5}$ using T_c^{mid},[21] and even using T_c^{onset}.[22] This result demonstrates the robustness of superconductivity in our $FeSe_{0.5}Te_{0.5}$ thin films under magnetic fields.

Finally, we evaluate the potential critical-current density of $FeSe_{0.5}Te_{0.5}$ for the application to thin-film conductors. The excellent properties observed in film C1 suggests that this film can show a high critical current density (J_c) in a superconducting state. We performed resistivity measurements with different excitation currents in the region below $T = 15$ K at $\mu_0 H = 0$, 1, 10, and 14 T. Part of the data at $\mu_0 H = 14$ T in $H \parallel c$ configuration is shown in Figs. 3(a) and 3(b). J_c is defined as the current density at which a finite electric field of 1 μVcm^{-1} emerges. The field-dependence of J_c is summarized in Fig. 3(c) at selected temperatures with

the reported J_c values on several materials. It is clearly seen that at T = 10 K, J_c of film C1 is one order of magnitude higher than that of $FeSe_{0.5}Te_{0.5}$ crystal,[22] and approaches the value reported by Iida *et al.* for $BaFe_{1.8}Co_{0.2}As_2$ thin films,[23] even though the value is still lower than that reported by Lee *et al.*[24] The most remarkable feature is that J_c is suppressed very slowly above 10 T. At T = 4.5 K, J_c roughly equals 5.9×10^4 Acm^{-2} at $\mu_0 H = 10$ T, and 4.2×10^4 Acm^{-2} at $\mu_0 H = 14$ T. The latter value is larger than that of MgB_2 thin films by almost one order of magnitude,[25] which suggests that iron-chalcogenide superconductor thin films have high potential under high-magnetic fields. It should also be noted that the present film is a pristine film simply prepared on CaF_2 without buffer layers. There is room for further improvement of J_c by introducing an external pinning center to the film, which may push up the critical current density to above 10^5 Acm^{-2} in high field regions.

To summarize, we have grown $FeSe_{0.5}Te_{0.5}$ thin films on a CaF_2 (100) substrate, and succeeded in obtaining films showing T_c as high as 15 K with sufficiently high reproducibility. The structural analysis indicates that the films are compressed along the a-axis. The high critical current density is also demonstrated. The value of J_c reaches 5.9×10^4 Acm^{-2} at T = 4.5 K and $\mu_0 H = 10$ T, which is comparable to that of Co-doped $BaFe_2As_2$ thin films. Better superconductivity has been recently confirmed in NdFeAs(O,F) thin films prepared on the same substrate material,[26] which indicates the common advantage of using CaF_2 to grow iron-based superconductor thin films.

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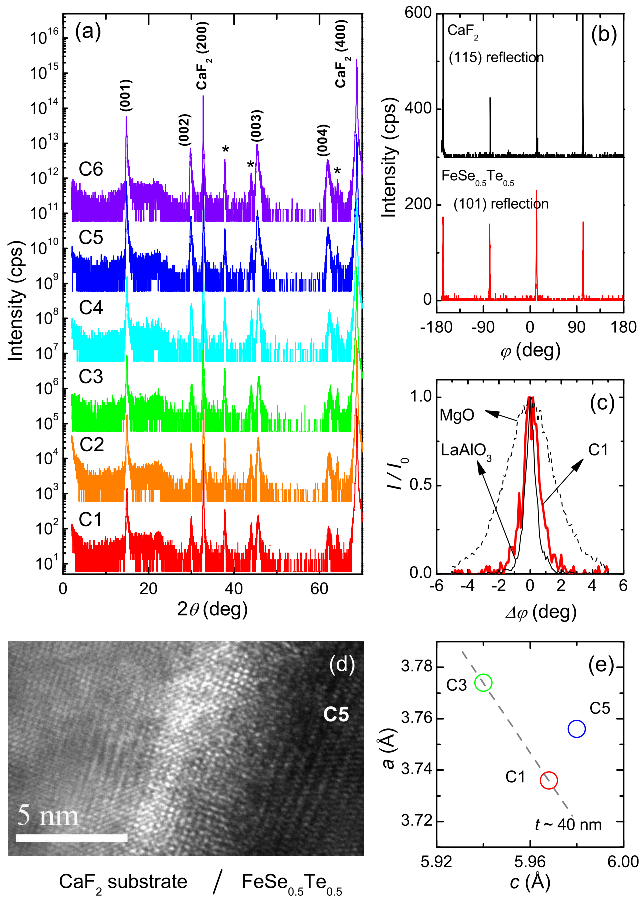

Fig. 1. (color online) (a) X-ray diffractions of six $FeSe_{0.5}Te_{0.5}$ thin films grown on CaF_2 (100). The origin of the vertical axis is shifted for each film. $*$ indicates peaks from an aluminum holder. (b) ϕ-scans of the 101 reflection of film C1 and the 115 reflection of CaF_2 substrate. (c) Comparison of the 101 reflections of film C1 with the films on $LaAlO_3$ and MgO in Ref. 18). (d) Cross-sectional TEM image at the interface of CaF_2 and film C5. (e) c-axis length vs a-axis length of films C1, C3, and C5. The dashed line is a guide to the eye.

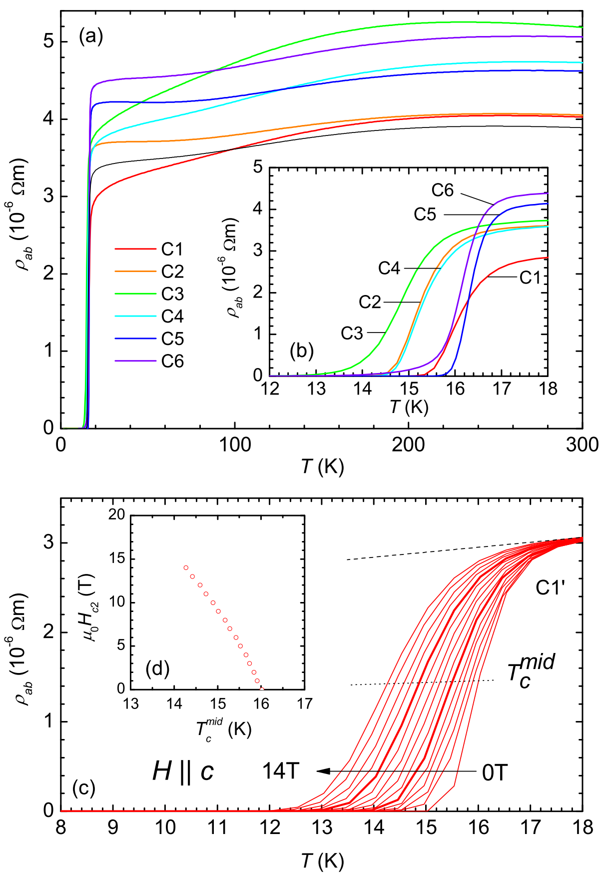

Fig. 2. (color online) (a) Temperature dependence of resistivity of six thin films grown on CaF_2, and (b) its closeup around T_c. (c) ρ-vs-T measured for film C1' under magnetic fields up to $\mu_0 H$ = 14 T applied along the c-axis.[20] The dashed line indicates normal-state resistivity, and the dotted line indicates the position of half of the normal resistivity. (d) T_c^{mid}-vs-H_{c2} plot of film C1' .

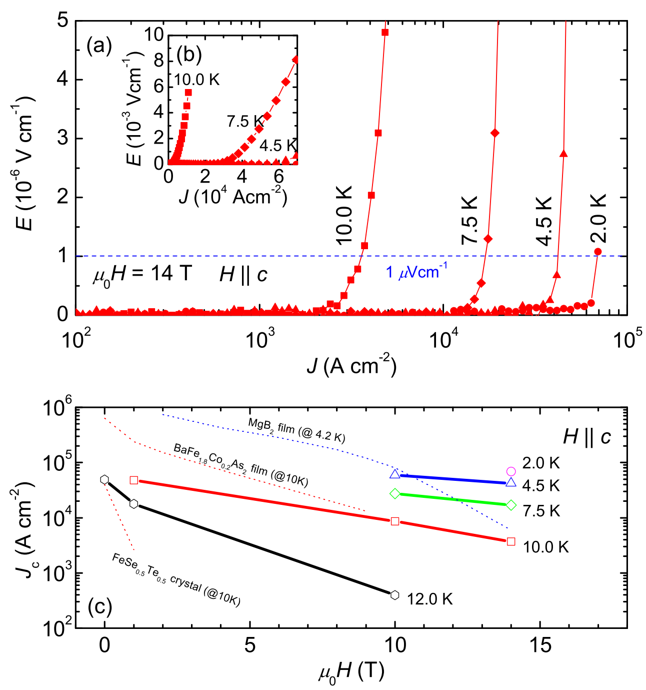

Fig. 3. (color online) (a) Current-density dependence of electric field in film C1. The maximum current available in PPMS is 5 mA corresponding to $J \approx 7 \times 10^4$ Acm^{-2}. (b) Large-scale plot of the same data. (c) Applied-field dependence of J_c at T = 2.0, 4.5, 7.5, 10.0, and 12.0 K. The data for $FeSe_{0.5}Te_{0.5}$ crystal,[22] $BaFe_{1.8}Co_{0.2}As_2$ thin film,[23] and MgB_2 thin film[25] are also plotted.